

## PATENT ABSTRACTS OF JAPAN

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(21)Application number : 2002-352999 (71)Applicant : HONDA MOTOR CO LTD  
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**(54) ELECTRODE STRUCTURE FOR SOLID POLYMER FUEL CELL AND ITS MANUFACTURING METHOD**

**(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide an electrode structure for a solid polymer fuel cell and its manufacturing method having a high reaction efficiency of a catalyst capable of establishing a high output and high efficiency.

**SOLUTION:** A 1st laminate having a 1st anode catalyst layer and a 1st cathode catalyst layer formed on both sides of a polymer electrolyte film is produced, and a 2nd laminate having a 2nd anode catalyst layer formed on an anode diffusion layer is produced. The 1st and the 2nd laminates are joined to each other so that the 1st anode catalyst layer of the 1st laminate comes into contact with the 2nd anode catalyst layer of the 2nd laminates. A 3rd laminate having a 2nd cathode catalyst layer formed on a cathode diffusion layer is produced, and the 1st and the 3rd laminates are joined each other so that the 1st cathode catalyst layer of the 1st laminate comes into contact with a 3rd cathode catalyst layer of the 3rd laminate.

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## CLAIMS

[Claim(s)]

[Claim 11]

[Claim 1] In the electrode structure for polymer electrolyte fuel cells which carried out the laminating of the cathode to the anode which carried out the laminating of the 1st catalyst bed, 2nd catalyst bed, and diffusion layer to the polyelectrolyte film in this sequence, and the opposite hand of said polyelectrolyte film,

The electrode structure for polymer electrolyte fuel cells characterized by making the void content of said 2nd catalyst bed larger than the void content of said 1st catalyst bed.

**Claim 2]**

[Claim 2] Said cathode is the electrode structure for polymer electrolyte fuel cells according to claim 1 characterized by having come to carry out the laminating of the 1st catalyst bed, 2nd catalyst bed, and diffusion layer to the polyelectrolyte film in this sequence, and making the void content of said 2nd catalyst bed larger than the void content of said 1st catalyst bed.

[Claim 3]

[Claim 5] The 1st layered product in which the 1st anode catalyst bed and the 1st cathode catalyst bed were formed to both sides of the polyelectrolyte film is produced.

The 2nd layered product in which the 2nd anode catalyst bed was formed on the front face of an anode diffusion layer is produced.

The manufacture approach of the electrode structure for polymer electrolyte fuel cells characterized by joining the said 1st and 2nd layered product mutually so that said 1st anode catalyst bed of said 1st layered product and said 2nd anode catalyst bed of said 2nd layered product may touch.

[Claim 4]

[Claim 1]  
The 3rd layered product in which the 2nd cathode catalyst bed was formed on the front face of a cathode diffusion layer is produced,

The manufacture approach of the electrode structure for polymer electrolyte fuel cells according to claim 3 characterized by joining the said 1st and 3rd layered product mutually so that said 1st cathode catalyst bed of said 1st layered product and said 3rd cathode catalyst bed of said 3rd layered product may touch.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]****[Field of the Invention]**

This invention relates to the electrode structure for polymer electrolyte fuel cells, and relates to the electrode structure for polymer electrolyte fuel cells which raised the reaction effectiveness of a catalyst especially, and its manufacture approach.

**[0002]****[Description of the Prior Art]**

A polymer electrolyte fuel cell is plate-like membrane electrode complex (MEA:Membrane Ele-).  
ctrode The laminating of the separator is carried out and it is constituted by the both sides of Assembly. Membrane electrode complex is a layered product by which the polyelectrolyte film was sandwiched between the electrode catalyst bed by the side of a cathode, and the electrode catalyst bed by the side of an anode, and the laminating of the gaseous diffusion layer was generally carried out to the outside of each electrode catalyst bed, respectively. If a oxidizing gas is passed to the gas passageway of the separator which was allotted to the gas passageway of the separator allotted to the anode side in hydrogen gas at the sink and cathode side, for example according to such a fuel cell, electrochemical reaction will occur and a current will occur.

**[0003]**

A gaseous diffusion layer diffuses fuel gas and a oxidizing gas in it at the same time it makes the electron generated according to electrochemical reaction transmit between an electrode catalyst bed and a separator during actuation of a fuel cell. Moreover, the electrode catalyst bed by the side of an anode makes fuel gas cause a chemical reaction, and makes it generate a proton (H<sup>+</sup>) and an electron, the electrode catalyst bed by the side of a cathode generates water from oxygen, a proton, and an electron, and an electrolyte membrane carries out ionic conduction of the proton. And power is taken out through the electrode catalyst bed of positive/negative. Here, what mixed the carbon particle with which the catalyst bed supported catalyst particles, such as Pt, and the electrolyte which consists of an ion conductive polymer is known (for example, patent reference 1 reference).

**[0004]****[Patent reference 1]**

JP,2000-243404,A (2 pages)

**[0005]****[Problem(s) to be Solved by the Invention]**

However, the catalyst metal is expensive, and although it is necessary to decrease the amount used, if the amount used is decreased, generation efficiency will fall.

**[0006]**

Then, this invention is made in view of the above-mentioned actual condition, and aims at offering the electrode structure for polymer electrolyte fuel cells which can attain high power and a well head with the catalyst metal of the minimal dose, and its manufacture approach.

**[0007]****[Means for Solving the Problem]**

The electrode structure for polymer electrolyte fuel cells of this invention is characterized by making the void content of the 2nd catalyst bed larger than the void content of said 1st catalyst bed in the electrode structure for polymer electrolyte fuel cells which carried out the laminating of the cathode to the anode which carried out the laminating of the 1st catalyst bed, 2nd catalyst bed, and diffusion layer in this

sequence at the polyelectrolyte film, and the opposite hand of the polyelectrolyte film.

[0008]

According to this invention, since the void content of the 2nd catalyst bed by the side of a diffusion layer is large, the permeability of a fuel is good and is smoothly supplied to the 1st catalyst bed. On the other hand, in the 1st catalyst bed by the side of the polyelectrolyte film, since a void content is low and precise, the contact frequency of a fuel and a catalyst metal is high, therefore the reaction which generates a proton from a fuel is promoted. Therefore, the catalyst metal of the minimal dose can attain high power and a well head.

[0009]

Here, as for a cathode, it is desirable to be able to carry out the laminating of the 1st catalyst bed, 2nd catalyst bed, and diffusion layer, to be able to constitute them from this sequence on the polyelectrolyte film, and to make the void content of the 2nd catalyst bed like an anode, larger than the void content of the 1st catalyst bed also in such a case. In such a mode, since the void content of the 1st catalyst bed is low and precise, the contact frequency of a proton and oxygen, and a catalyst metal is high, therefore the reaction which generates water from a proton and oxygen is promoted. Moreover, in the 2nd catalyst bed, the water generated since the void content was large is discharged promptly.

[0010]

Next, the manufacture approach of the electrode structure for polymer electrolyte fuel cells of this invention The 1st layered product in which the 1st anode catalyst bed and the 1st cathode catalyst bed were formed to both sides of the polyelectrolyte film is produced. The 2nd layered product in which the 2nd anode catalyst bed was formed on the front face of an anode diffusion layer is produced, and it is characterized by joining the 1st and 2nd layered product mutually so that the 1st anode catalyst bed of the 1st layered product and the 2nd anode catalyst bed of the 2nd layered product may touch.

[0011]

In the above manufacture approaches, since the catalyst bed of an anode can be constituted in two or more layers, the optimal property for each catalyst bed can be given. For example, the void content of the 2nd catalyst bed can be made larger than the void content of said 1st catalyst bed as mentioned above. Or the amount and class of catalyst metal are also changeable by the 1st and 2nd catalyst bed.

[0012]

Here, the above manufacture approaches are applicable also to a cathode. That is, the 3rd layered product in which the 2nd cathode catalyst bed was formed on the front face of a cathode diffusion layer is produced, and the 1st and 3rd layered product is mutually joined so that the 1st cathode catalyst bed of the 1st layered product and the 3rd cathode catalyst bed of the 3rd layered product may touch.

[0013]

[Example]

Next, with reference to the example and the example of a comparison of the electrode structure for polymer electrolyte fuel cells of this invention, the effectiveness of this invention is explained concretely.

<Example 1>

#### 1. Production of Electrolysis Film-Electrode Complex

2.5g (trade name: VGCF, Showa Denko K.K. make) of crystalline carbon fibers was mixed with 10g (trade name: TEC10E50E, Tanaka Kikinzoku Kogyo make) of platinum support carbon particles which set the weight ratio of ion conductive polymer (trade name: NafionSE20192, product made from Dupont) 35g, and carbon black and platinum to 50:50, and it considered as the cathode catalyst paste. Spreading desiccation of this cathode catalyst paste was carried out so that the amount of Pt(s) might serve as 0.3 mg/cm<sup>2</sup> on an FEP sheet, and it considered as the cathode electrode sheet (for the 1st cathode catalyst bed).

[0014]

10g (trade name: TEC 61E54, Pt:Ru=1:1, Tanaka Kikinzoku Kogyo make) of Pt-Ru support carbon particles which set the weight ratio of ion conductive polymer (trade name: NafionSE20192, product made from Dupont) 36.8g, and a carbon black and a catalyst to 46:54 was mixed, and it considered as the anode catalyst paste. Spreading desiccation of this anode catalyst paste was carried out so that the amount of catalysts might serve as 0.2 mg/cm<sup>2</sup> on an FEP sheet, and it considered as the anode electrode sheet (for the 1st anode catalyst bed). These cathode electrode sheet and the anode electrode sheet were imprinted on the electrolysis film by the decal method, and electrolysis film-electrode complex was produced.

[0015]

#### 2. Production of Cathode Diffusion Layer

2.5g (VGCF: Showa Denko make) of crystalline carbon fibers was mixed to 10g (TEC10E50E, Tanaka Kikinzoku Kogyo make) of platinum support carbon particles which set the weight ratio of ion conductive

polymer (trade name: NafionSE5112, product made from Dupont) 100g, carbon black, and platinum to 50:50, and it considered as the substrate layer paste C (for the 2nd cathode catalyst bed). Moreover, 18g (trade name: made in [ Cabot ] the Balkan Peninsula XC75) of carbon black powder was mixed with 12g (trade name: L170J, Asahi Glass Co., Ltd. make) of Teflon (trademark) powder to ethylene glycol, and it considered as the substrate layer paste B.

[0016]

After applying and calcinating the substrate layer paste B on the carbon paper (trade name: TGP060, Toray Industries, Inc. make) given a water-repellent finish beforehand so that it may become 2.3 mg/cm<sup>2</sup>, spreading desiccation of the substrate layer paste C was carried out so that catalyst coverage might serve as 0.1 mg/cm<sup>2</sup>, and the cathode diffusion layer was created.

[0017]

### 3. Creation of Anode Diffusion Layer

2.3g (VGCF: Showa Denko make) of crystalline carbon fibers was mixed to 10g (trade name: TEC 61E54, Pt:Ru=1:1, Tanaka Kikinzoku Kogyo make) of Pt-Ru support carbon particles which set the weight ratio of ion conductive polymer (trade name: NafionSE5112, product made from Dupont) 100g, and a carbon black and a catalyst to 46:54, and it considered as the substrate layer paste A (for the 2nd anode catalyst bed). Moreover, 18g (trade name: made in [ Cabot ] the Balkan Peninsula XC75) of carbon black powder was mixed to ethylene glycol at 12g (trade name: L170J, Asahi Glass Co., Ltd. make) of Teflon (trademark) powder, and it considered as the substrate layer paste B (it is the same as the above-mentioned substrate layer paste B).

[0018]

After applying and calcinating the substrate layer paste B on the carbon paper (TGP060, Toray Industries make) given a water-repellent finish beforehand so that it may become 2.3 mg/cm<sup>2</sup>, spreading desiccation of the substrate layer paste A was carried out so that 0.1mg /might be set to 2 cm in the amount of catalysts, and it considered as the anode diffusion layer.

[0019]

### 4. Production of Electrode Structure

After having arranged the cathode diffusion layer to the cathode pole of the above-mentioned electrolysis film-electrode complex and having arranged the anode diffusion layer to the anode pole, it unified in hot pressing and considered as the electrode structure of an example 1.

[0020]

<The example 1 of a comparison>

#### 1. Production of Electrolysis Film-Electrode Complex

2.5g (trade name: VGCF, Showa Denko K.K. make) of crystalline carbon fibers was mixed to 10g (trade name: TEC10E50E, Tanaka Kikinzoku Kogyo make) of platinum support carbon particles which set the weight ratio of ion conductive polymer (trade name: NafionSE20192, product made from Dupont) 35g, and carbon black and platinum to 50:50, and it considered as the cathode catalyst paste.

[0021]

After applying and drying the substrate layer paste C used in the example 1 on the FEP sheet so that the amount of Pt(s) may serve as 0.1 mg/cm<sup>2</sup>, on it, further, spreading desiccation was carried out so that the amount of Pt(s) might serve as 0.3 mg/cm<sup>2</sup>, and the above-mentioned cathode catalyst paste was used as the cathode electrode sheet.

[0022]

10g (trade name: TEC 61E54, Pt:Ru=1:1, Tanaka Kikinzoku Kogyo make) of Pt-Ru support carbon particles which set the weight ratio of ion conductive polymer (trade name: NafionSE20192, product made from Dupont) 36.8g, and a carbon black and a catalyst to 46:54 was mixed, and it considered as the anode catalyst paste.

[0023]

After carrying out spreading desiccation of the substrate layer paste A used in the example 1 on the FEP sheet so that it may become 0.1 mg/cm<sup>2</sup> in the amount of catalysts, on it, further, spreading desiccation was carried out so that the amount of catalysts might serve as 0.2 mg/cm<sup>2</sup>, and the above-mentioned anode catalyst paste was used as the anode electrode sheet. The above-mentioned cathode electrode sheet and the anode electrode sheet were imprinted on the electrolysis film by the decal method, and electrolysis film-electrode complex was obtained.

[0024]

### 2. Production of Electrode Structure

The substrate layer paste B used for the carbon paper given a water-repellent finish beforehand in the example 1 was applied and calcinated by 2.3 mg/cm<sup>2</sup>, the diffusion layer was produced, the above-mentioned electrolysis film-electrode complex was put by this diffusion layer, and it considered as the electrode structure of the example 1 of a comparison.

[0025]

<The example 2 of a comparison>

### 1. Creation of Cathode Electrode

After applying and calcinating the substrate layer paste B which used in the example 1 on the carbon paper (trade name: TGP060, Toray Industries, Inc. make) given a water-repellent finish beforehand by 2.3 mg/cm<sup>2</sup>, the spreading desiccation of the cathode catalyst paste which used further the substrate layer paste A used in the example 1 in the example 1 after spreading / desiccation so that catalyst coverage might serve as 0.1 mg/cm<sup>2</sup> carried out so that the amount of Pt(s) may serve as 0.3 mg/cm<sup>2</sup>, and it considered as a cathode electrode.

[0026]

### 2. Creation of Anode Electrode

After applying and calcinating the substrate layer paste B which used in an example 1 on the carbon paper (trade name: TGP060, Toray Industries, Inc. make) given a water-repellent finish beforehand so that it may become 2.3 mg/cm<sup>2</sup>, the spreading desiccation of the anode catalyst paste which used further the substrate layer paste C used in the example 1 in the example 1 after spreading desiccation so that catalyst coverage might serve as 0.1 mg/cm<sup>2</sup> carried out so that the amount of catalysts may serve as 0.3 mg/cm<sup>2</sup>, and it considered as an anode electrode.

[0027]

### 3. Production of Electrode Structure

The electrolysis film was put and the above-mentioned cathode electrode and the anode electrode were made into the electrode structure of the example 2 of a comparison.

[0028]

<The example 3 of a comparison>

### 1. Production of Electrolysis Film-Electrode Complex

2.5g (VGCF: Showa Denko make) of crystalline carbon fibers was mixed to 10g (TEC10E50E, Tanaka Kikinzoku Kogyo make) of platinum support carbon particles which set the weight ratio of ion conductive polymer (trade name: NafionSE20192, product made from Dupont) 35g, and carbon black and platinum to 50:50, and it considered as the cathode catalyst paste. This cathode catalyst paste was applied and dried so that the amount of Pt(s) might serve as 0.3 mg/cm<sup>2</sup> on an FEP sheet, and it considered as the cathode electrode sheet.

[0029]

10g (trade name: TEC 61E54, Pt:Ru=1:1, Tanaka Kikinzoku Kogyo make) of Pt-Ru support carbon particles which set the weight ratio of ion conductive polymer (trade name: NafionSE20192, product made from Dupont) 36.8g, and a carbon black and a catalyst to 46:54 was mixed, and it considered as the anode catalyst paste. This anode catalyst paste was applied and dried so that the amount of catalysts might serve as 0.2 mg/cm<sup>2</sup> on an FEP sheet, and it considered as the anode electrode sheet. These cathode electrode sheet and the anode electrode sheet were imprinted on the electrolysis film by the decal method, and electrolysis film-electrode complex was produced.

[0030]

### 2. Production of Cathode Diffusion Layer

10g (trade name: TEC10E50E, Tanaka Kikinzoku Kogyo make) of platinum support carbon particles which set the weight ratio of ion conductive polymer (trade name: NafionSE5112, product made from Dupont) 100g, carbon black, and platinum to 50:50 was mixed, and it considered as the substrate layer paste C2.

[0031]

18g (trade name: made in [ Cabot ] the Balkan Peninsula XC75) of carbon black powder was mixed to ethylene glycol at 12g (trade name: L170J, Asahi Glass Co., Ltd. make) of Teflon (trademark) powder, and it considered as the substrate layer paste B.

[0032]

After applying and calcinating the substrate layer paste B by 2.3 mg/cm<sup>2</sup> on the carbon paper (trade name: TGP060:Toray Industries, Inc. make) given a water-repellent finish beforehand, the substrate layer paste C used in the example 1 was applied and dried so that catalyst coverage might serve as 0.1 mg/cm<sup>2</sup>, and the cathode diffusion layer was created.

[0033]

## 3. Creation of Anode Diffusion Layer

10g (trade name: TEC 61E54, Pt:Ru=1:1, Tanaka Kikinzoku Kogyo make) of Pt-Ru support carbon particles which set the weight ratio of ion conductive polymer (trade name: NafionSE5112, product made from Dupont) 100g, and a carbon black and a catalyst to 46:54 was mixed, and it considered as the substrate layer paste A2.

[0034]

18g (product made from Balkan Peninsula XC75:Cabot) of carbon black powder was mixed to ethylene glycol at 12g (trade name: L170J, Asahi Glass Co., Ltd. make) of Teflon (trademark) powder, and it considered as the substrate layer paste B.

[0035]

After applying and calcinating the substrate layer paste B by 2.3 mg/cm<sup>2</sup> on the carbon paper (trade name: TGP060, Toray Industries, Inc. make) given a water-repellent finish beforehand, the above-mentioned substrate layer paste A2 was applied and dried so that it might become 0.1 mg/cm<sup>2</sup> in the amount of catalysts, and it considered as the anode diffusion layer.

[0036]

## 4. Production of Electrode Structure

After having arranged the cathode diffusion layer to the cathode pole of the above-mentioned electrolysis film-electrode complex and having arranged the anode diffusion layer to the anode pole, it unified in hot pressing and considered as the electrode structure of the example 3 of a comparison.

[0037]

## &lt;Measurement of terminal voltage&gt;

Each electrode structure of the example produced as mentioned above and the example of a comparison carries out the laminating of the 1st anode catalyst bed, the 2nd anode catalyst bed, a hydrophobic layer and a diffusion layer, and the 1st cathode catalyst bed, the 2nd cathode catalyst bed, a hydrophobic layer and a diffusion layer to the both sides of the electrolysis film in this sequence. The void content of each catalyst bed is shown in a table 1.

[0038]

[A table 1]

	気孔率 (%)			
	第1のカソード 触媒層	第2のカソード 触媒層	第1のアノード 触媒層	第2のアノード 触媒層
実施例 1	7 5	8 5	6 2	8 5
比較例 1	7 5	7 2	6 2	6 1
比較例 2	8 5	8 5	6 5	6 5
比較例 3	7 5	6 2	6 2	6 0

[0039]

Next, a utilization factor [ in / to the fuel cell incorporating the above-mentioned electrode structure / cell temperature:80 degree C, amount of humidification:anode 45RH%, cathode 85RH%, and 0.5 A/cm<sup>2</sup> ]: Anode 60%, pure hydrogen was supplied to the anode under cathode 60% conditions, and change of the terminal voltage when changing current density was investigated. The result is shown in drawing 1 .

[0040]

There is little lowering of the terminal voltage at the time of making current density increase in the example with the larger void content of the 2nd catalyst bed than the void content of the 1st catalyst bed so that drawing 1 may show. This shows that the reaction effectiveness of a catalyst can attain high power and a well head highly with the electrode structure of this invention.

[0041]

[Effect of the Invention]

As explained above, since the void content of the 2nd catalyst bed by the side of a diffusion layer was made larger than the void content of the 1st catalyst bed by the side of the electrolysis film, according to this invention, the reaction effectiveness of a catalyst can attain high power and a well head highly.

[Brief Description of the Drawings]

[Drawing 1] It is the diagram showing the relation of the current density and terminal voltage in the example of this invention.

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[Translation done.]

## \* NOTICES \*

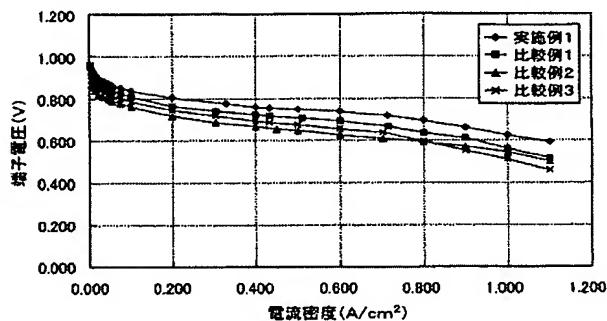
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DRAWINGS

## [Drawing 1]



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[Translation done.]

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**SOLUTION:** A 1st laminate having a 1st anode catalyst layer and a 1st cathode catalyst layer formed on both sides of a polymer electrolyte film is produced, and a 2nd laminate having a 2nd anode catalyst layer formed on an anode diffusion layer is produced. The 1st and the 2nd laminates are joined to each other so that the 1st anode catalyst layer of the 1st laminate comes into contact with the 2nd anode catalyst layer of the 2nd laminates. A 3rd laminate having a 2nd cathode catalyst layer formed on a cathode diffusion layer is produced, and the 1st and the 3rd laminates are joined each other so that the 1st cathode catalyst layer of the 1st laminate comes into contact with a 3rd cathode catalyst layer of the 3rd laminate.

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最終頁に続く

(54) 【発明の名称】 固体高分子型燃料電池用電極構造体およびその製造方法

## (57) 【要約】

【課題】触媒の反応効率が高く、高出力かつ高効率を達成することができる固体高分子型燃料電池用電極構造体およびその製造方法を提供する。

【解決手段】高分子電解質膜の両面に第1のアノード触媒層および第1のカソード触媒層を形成した第1の積層体を作製し、アノード拡散層の表面に第2のアノード触媒層を形成した第2の積層体を作製する。第1の積層体の第1のアノード触媒層と第2の積層体の前記第2のアノード触媒層とが接するように第1、第2の積層体どうしを互いに接合する。カソード拡散層の表面に第2のカソード触媒層を形成した第3の積層体を作製し、第1の積層体の第1のカソード触媒層と第3の積層体の第3のカソード触媒層とが接するように第1、第3の積層体どうしを互いに接合する。

【選択図】 なし

## 【特許請求の範囲】

## 【請求項 1】

高分子電解質膜に、第1の触媒層、第2の触媒層および拡散層をこの順番で積層したアノードと、前記高分子電解質膜の反対側にカソードを積層した固体高分子型燃料電池用電極構造体において、前記第2の触媒層の空孔率を前記第1の触媒層の空孔率よりも大きくしたことを特徴とする固体高分子型燃料電池用電極構造体。

## 【請求項 2】

前記カソードは、高分子電解質膜に、第1の触媒層、第2の触媒層および拡散層をこの順番で積層してなり、前記第2の触媒層の空孔率を前記第1の触媒層の空孔率よりも大きく 10 したことを特徴とする請求項1に記載の固体高分子型燃料電池用電極構造体。

## 【請求項 3】

高分子電解質膜の両面に第1のアノード触媒層および第1のカソード触媒層を形成した第1の積層体を作製し、アノード拡散層の表面に第2のアノード触媒層を形成した第2の積層体を作製し、前記第1の積層体の前記第1のアノード触媒層と前記第2の積層体の前記第2のアノード触媒層とが接するように前記第1、第2の積層体どうしを互いに接合することを特徴とする固体高分子型燃料電池用電極構造体の製造方法。

## 【請求項 4】

カソード拡散層の表面に第2のカソード触媒層を形成した第3の積層体を作製し、前記第1の積層体の前記第1のカソード触媒層と前記第3の積層体の前記第3のカソード触媒層とが接するように前記第1、第3の積層体どうしを互いに接合することを特徴とする請求項3に記載の固体高分子型燃料電池用電極構造体の製造方法。

## 【発明の詳細な説明】

## 【0001】

## 【発明の属する技術分野】

本発明は、固体高分子型燃料電池用電極構造体に係り、特に、触媒の反応効率を向上させた固体高分子型燃料電池用電極構造体およびその製造方法に関するものである。

## 【0002】

## 【従来の技術】

固体高分子型燃料電池は、平板状の膜電極複合体 (MEA : Membrane Electrode Assembly) の両側にセパレータが積層されて構成されている。膜電極複合体は、一般に、カソード側の電極触媒層とアノード側の電極触媒層との間に高分子電解質膜が挟まれ、各電極触媒層の外側にガス拡散層がそれぞれ積層された積層体である。このような燃料電池によると、例えば、アノード側に配されたセパレータのガス通路に水素ガスを流し、カソード側に配されたセパレータのガス通路に酸化性ガスを流すと、電気化学反応が起こって電流が発生する。

## 【0003】

燃料電池の作動中においては、ガス拡散層は電気化学反応によって生成した電子を電極触媒層とセパレータとの間で伝達させると同時に燃料ガスおよび酸化性ガスを拡散させる。また、アノード側の電極触媒層は燃料ガスに化学反応を起こさせプロトン ( $H^+$ ) と電子を発生させ、カソード側の電極触媒層は酸素とプロトンと電子から水を生成し、電解質膜はプロトンをイオン伝導させる。そして、正負の電極触媒層を通して電力が取り出される。ここで、触媒層は、Pt等の触媒粒子を担持したカーボン粒子と、イオン導伝性ポリマーからなる電解質とを混合したものが知られている (例えば、特許文献1参照)。

## 【0004】

## 【特許文献1】

特開2000-243404号公報 (2頁)

## 【0005】

## 【発明が解決しようとする課題】

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しかしながら、触媒金属は高価であり使用量を減少させる必要があるが、使用量を減少させると発電効率が低下する。

【0006】

そこで、本発明は、上記実情に鑑みてなされたものであって、最小量の触媒金属で高出力かつ高効率を達成することができる固体高分子型燃料電池用電極構造体およびその製造方法を提供することを目的としている。

【0007】

【課題を解決するための手段】

本発明の固体高分子型燃料電池用電極構造体は、高分子電解質膜に、第1の触媒層、第2の触媒層および拡散層をこの順番で積層したアノードと、高分子電解質膜の反対側にカソードを積層した固体高分子型燃料電池用電極構造体において、第2の触媒層の空孔率を前記第1の触媒層の空孔率よりも大きくしたことを特徴としている。10

【0008】

本発明によれば、拡散層側の第2の触媒層の空孔率が大きいため、燃料の浸透性が良好で第1の触媒層にスムーズに供給される。一方、高分子電解質膜側の第1の触媒層では、空孔率が低く緻密なため燃料と触媒金属との接触頻度が高く、したがって燃料からプロトンを発生する反応が促進される。したがって、最小量の触媒金属で高出力かつ高効率を達成することができる。

【0009】

ここで、カソードは、アノードと同様に高分子電解質膜に、第1の触媒層、第2の触媒層および拡散層をこの順番で積層して構成することができ、その場合にも第2の触媒層の空孔率を第1の触媒層の空孔率よりも大きくすることが望ましい。このような態様においては、第1の触媒層の空孔率が低く緻密なためプロトンおよび酸素と触媒金属との接触頻度が高く、したがってプロトンと酸素から水を発生する反応が促進される。また、第2の触媒層では、空孔率が大きいため発生した水が速やかに排出される。20

【0010】

次に、本発明の固体高分子型燃料電池用電極構造体の製造方法は、高分子電解質膜の両面に第1のアノード触媒層および第1のカソード触媒層を形成した第1の積層体を作製し、アノード拡散層の表面に第2のアノード触媒層を形成した第2の積層体を作製し、第1の積層体の第1のアノード触媒層と第2の積層体の第2のアノード触媒層とが接するように第1、第2の積層体どうしを互いに接合することを特徴としている。30

【0011】

上記のような製造方法においては、アノードの触媒層を複数層に構成することができるから、各触媒層に最適な特性を付与することができる。たとえば、前述のように、第2の触媒層の空孔率を前記第1の触媒層の空孔率よりも大きくすることができる。あるいは、第1、第2の触媒層で触媒金属の量や種類を変えることもできる。

【0012】

ここで、カソードにも上記のような製造方法を適用することができる。すなわち、カソード拡散層の表面に第3のカソード触媒層を形成した第3の積層体を作製し、第1の積層体の第1のカソード触媒層と第3の積層体の第3のカソード触媒層とが接するように第1、第3の積層体どうしを互いに接合する。40

【0013】

【実施例】

次に、本発明の固体高分子型燃料電池用電極構造体の実施例および比較例を参照して本発明の効果を具体的に説明する。

〈実施例1〉

1. 電解膜-電極複合体の作製

イオン導伝性ポリマー（商品名：Nafion SE 20192、DuPont社製）35gと、カーボンブラックと白金の重量比を50:50とした白金担持カーボン粒子（商品名：TEC10E50E、田中貴金属工業社製）10gと、結晶性炭素纖維（商品名：V 50

G C F、昭和電工社製) 2. 5 gとを混合し、カソード触媒ペーストとした。このカソード触媒ペーストをF E Pシート上にPt量が0. 3 mg/cm<sup>2</sup>となるように塗布乾燥し、カソード電極シート(第1のカソード触媒層用)とした。

【0014】

イオン導伝性ポリマー(商品名: Nafion SE 20192、Dupont社製) 36. 8 gと、カーボンブラックと触媒の重量比を46:54としたPt-Ru担持カーボン粒子(商品名: TEC 61 E 54、Pt:Ru=1:1、田中貴金属工業社製) 10 gとを混合し、アノード触媒ペーストとした。このアノード触媒ペーストをF E Pシート上に触媒量が0. 2 mg/cm<sup>2</sup>となるように塗布乾燥し、アノード電極シート(第1のアノード触媒層用)とした。これらカソード電極シートおよびアノード電極シートをデカール法によって電解膜に転写し、電解膜-電極複合体を作製した。  
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【0015】

2. カソード拡散層の作製

イオン導伝性ポリマー(商品名: Nafion SE 5112、Dupont社製) 100 gとカーボンブラックと白金の重量比を50:50とした白金担持カーボン粒子(TEC 10 E 50 E、田中貴金属工業社製) 10 gに結晶性炭素繊維(V G C F:昭和電工製) 2. 5 gを混合し、下地層ペーストC(第2のカソード触媒層用)とした。また、エチレングリコールに、テフロン(登録商標)粉末(商品名: L 170 J、旭硝子社製) 12 gと、カーボンブラック粉末(商品名: バルカンXC 75、Cabot社製) 18 gとを混合し、下地層ペーストBとした。  
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【0016】

予め撥水処理したカーボンペーパー(商品名: TGP 060、東レ社製)上に、下地層ペーストBを2. 3 mg/cm<sup>2</sup>となるように塗布し焼成した後、下地層ペーストCを触媒塗布量が0. 1 mg/cm<sup>2</sup>となるように塗布乾燥し、カソード拡散層を作成した。

【0017】

3. アノード拡散層の作成

イオン導伝性ポリマー(商品名: Nafion SE 5112、Dupont社製) 100 gと、カーボンブラックと触媒の重量比を46:54としたPt-Ru担持カーボン粒子(商品名: TEC 61 E 54、Pt:Ru=1:1、田中貴金属工業社製) 10 gに結晶性炭素繊維(V G C F:昭和電工製) 2. 3 gを混合し、下地層ペーストA(第2のアノード触媒層用)とした。また、エチレングリコールにテフロン(登録商標)粉末(商品名: L 170 J、旭硝子社製) 12 gにカーボンブラック粉末(商品名: バルカンXC 75、Cabot社製) 18 gを混合し下地層ペーストB(前述の下地層ペーストBと同じ)とした。  
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【0018】

予め撥水処理したカーボンペーパー(TGP 060、東レ製)上に、下地層ペーストBを2. 3 mg/cm<sup>2</sup>となるように塗布し焼成した後、下地層ペーストAを触媒量で0. 1 mg/cm<sup>2</sup>となるように塗布乾燥し、アノード拡散層とした。

【0019】

4. 電極構造体の作製

前述の電解膜-電極複合体のカソード極にカソード拡散層、アノード極にアノード拡散層を配置した後、ホットプレス法にて一体化し実施例1の電極構造体とした。  
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【0020】

<比較例1>

1. 電解膜-電極複合体の作製

イオン導伝性ポリマー(商品名: Nafion SE 20192、Dupont社製) 35 gと、カーボンブラックと白金の重量比を50:50とした白金担持カーボン粒子(商品名: TEC 10 E 50 E、田中貴金属工業社製) 10 gに結晶性炭素繊維(商品名: V G C F:昭和電工社製) 2. 5 gを混合しカソード触媒ペーストとした。

【0021】

FEPシート上に実施例1で用いた下地層ペーストCをPt量が0.1mg/cm<sup>2</sup>となるよう塗布、乾燥した後、その上にさらに上記カソード触媒ペーストをPt量が0.3mg/cm<sup>2</sup>となるよう塗布乾燥し、カソード電極シートとした。

【0022】

イオン導伝性ポリマー（商品名：Nafion SE 20192、Dupont社製）36.8gと、カーボンブラックと触媒の重量比を46:54としたPt-Ru担持カーボン粒子（商品名：TEC61E54、Pt:Ru=1:1、田中貴金属工業社製）10gを混合しアノード触媒ペーストとした。

【0023】

FEPシート上に実施例1で用いた下地層ペーストAを触媒量で0.1mg/cm<sup>2</sup>となるよう塗布乾燥した後、その上にさらに上記アノード触媒ペーストを触媒量が0.2mg/cm<sup>2</sup>となるよう塗布乾燥し、アノード電極シートとした。上記カソード電極シートおよびアノード電極シートをデカール法により、電解膜に転写し、電解膜-電極複合体を得た。

【0024】

2. 電極構造体の作製

あらかじめ撥水処理したカーボンペーパーに実施例1で用いた下地層ペーストBを2.3mg/cm<sup>2</sup>で塗布・焼成して拡散層を作製し、この拡散層で上記電解膜-電極複合体を挟み込み、比較例1の電極構造体とした。

【0025】

<比較例2>

1. カソード電極の作成

あらかじめ撥水処理したカーボンペーパー（商品名：TGP060、東レ社製）上に実施例1で用いた下地層ペーストBを2.3mg/cm<sup>2</sup>で塗布・焼成した後、実施例1で用いた下地層ペーストAを触媒塗布量が0.1mg/cm<sup>2</sup>となるよう塗布・乾燥後、さらに、実施例1で用いたカソード触媒ペーストをPt量が0.3mg/cm<sup>2</sup>となるよう塗布乾燥し、カソード電極とした。

【0026】

2. アノード電極の作成

あらかじめ撥水処理したカーボンペーパー（商品名：TGP060、東レ社製）上に実施例1で用いた下地層ペーストBを2.3mg/cm<sup>2</sup>となるよう塗布・焼成した後、実施例1で用いた下地層ペーストCを触媒塗布量が0.1mg/cm<sup>2</sup>となるよう塗布乾燥後、さらに、実施例1で用いたアノード触媒ペーストを触媒量が0.3mg/cm<sup>2</sup>となるよう塗布乾燥し、アノード電極とした。

【0027】

3. 電極構造体の作製

上記カソード電極およびアノード電極を電解膜を挟み込み、比較例2の電極構造体とした。

【0028】

<比較例3>

1. 電解膜-電極複合体の作製

イオン導伝性ポリマー（商品名：Nafion SE 20192、Dupont社製）35gと、カーボンブラックと白金の重量比を50:50とした白金担持カーボン粒子（TEC10E50E、田中貴金属工業社製）10gに結晶性炭素繊維（VGC-F：昭和電工製）2.5gを混合しカソード触媒ペーストとした。このカソード触媒ペーストをFEPシート上にPt量が0.3mg/cm<sup>2</sup>となるよう塗布・乾燥し、カソード電極シートとした。

【0029】

イオン導伝性ポリマー（商品名：Nafion SE 20192、Dupont社製）36.8gと、カーボンブラックと触媒の重量比を46:54としたPt-Ru担持カーボン

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粒子（商品名：T E C 6 1 E 5 4、Pt : Ru = 1 : 1、田中貴金属工業社製）10 gを混合しアノード触媒ペーストとした。このアノード触媒ペーストをFEPシート上に触媒量が $0.2 \text{ mg/cm}^2$ となるように塗布・乾燥し、アノード電極シートとした。これらカソード電極シートおよびアノード電極シートをデカール法によって電解膜に転写し、電解膜-電極複合体を作製した。

【0030】

2. カソード拡散層の作製

イオン導伝性ポリマー（商品名：Nafion SE 5112、DuPont社製）100 gとカーボンブラックと白金の重量比を50:50とした白金担持カーボン粒子（商品名：T E C 1 0 E 5 0 E、田中貴金属工業社製）10 gを混合し、下地層ペーストC2とした。  
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【0031】

エチレングリコールにテフロン（登録商標）粉末（商品名：L170J、旭硝子社製）12 gにカーボンブラック粉末（商品名：バルカンXC75、Cabot社製）18 gを混合し下地層ペーストBとした。

【0032】

あらかじめ撥水処理したカーボンペーパー（商品名：TGP060：東レ社製）上に下地層ペーストBを $2.3 \text{ mg/cm}^2$ で塗布・焼成した後、実施例1で用いた下地層ペーストC2を触媒塗布量が $0.1 \text{ mg/cm}^2$ となるように塗布・乾燥し、カソード拡散層を作成した。  
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【0033】

3. アノード拡散層の作成

イオン導伝性ポリマー（商品名：Nafion SE 5112、DuPont社製）100 gと、カーボンブラックと触媒の重量比を46:54としたPt-Ru担持カーボン粒子（商品名：T E C 6 1 E 5 4、Pt : Ru = 1 : 1、田中貴金属工業社製）10 gを混合し、下地層ペーストA2とした。

【0034】

エチレングリコールにテフロン（登録商標）粉末（商品名：L170J、旭硝子社製）12 gにカーボンブラック粉末（バルカンXC75：Cabot社製）18 gを混合し下地層ペーストBとした。  
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【0035】

あらかじめ撥水処理したカーボンペーパー（商品名：TGP060、東レ社製）上に下地層ペーストBを $2.3 \text{ mg/cm}^2$ で塗布・焼成した後、上記下地層ペーストA2を触媒量で $0.1 \text{ mg/cm}^2$ となるように塗布・乾燥し、アノード拡散層とした。

【0036】

4. 電極構造体の作製

前述の電解膜-電極複合体のカソード極にカソード拡散層、アノード極にアノード拡散層を配置した後、ホットプレス法にて一体化し比較例3の電極構造体とした。

【0037】

<端子電圧の測定>

上記のようにして作製された実施例および比較例の電極構造体は、いずれも電解膜の両側に、第1のアノード触媒層、第2のアノード触媒層、撥水層および拡散層と、第1のカソード触媒層、第2のカソード触媒層、撥水層および拡散層とをこの順番で積層したものである。表1に各触媒層の空孔率を示す。  
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【0038】

【表1】

	気孔率 (%)			
	第1のカソード 触媒層	第2のカソード 触媒層	第1のアノード 触媒層	第2のアノード 触媒層
実施例 1	75	85	62	85
比較例 1	75	72	62	61
比較例 2	85	85	65	65
比較例 3	75	62	62	60

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## 【0039】

次に、上記電極構造体を組み込んだ燃料電池に対して、セル温度：80℃、加湿量：アノード45RH%、カソード85RH%、0.5A/cm<sup>2</sup>における利用率：アノード60%、カソード60%の条件下で純水素をアノードに供給し、電流密度を変化させたときの端子電圧の変化を調査した。その結果を図1に示す。

## 【0040】

図1から判るように、第2の触媒層の空孔率が第1の触媒層の空孔率よりも大きい実施例では、電流密度を増加させたときの端子電圧の低下が少ない。このことから、本発明の電極構造では、触媒の反応効率が高く高出力かつ高効率を達成することができる。

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## 【0041】

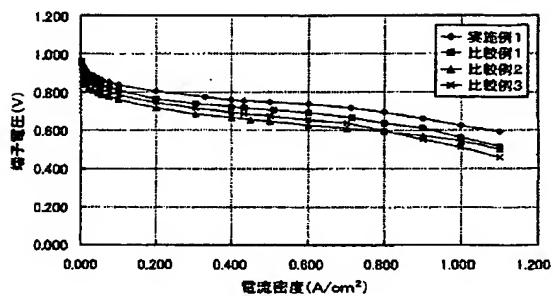
## 【発明の効果】

以上説明したように、本発明によれば、拡散層側の第2の触媒層の空孔率を電解膜側の第1の触媒層の空孔率よりも大きくしたから、触媒の反応効率が高く高出力かつ高効率を達成することができる。

## 【図面の簡単な説明】

【図1】本発明の実施例における電流密度と端子電圧との関係を示す線図である。

【図1】



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